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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Ambient and Elevated Temperature Curing Polymer
Compositions Useful for Aqueous Based Paints and Wood
Coatings

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Notice: This application is as filed and may therefore contain an
incomplete specification.



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AMBIENT AND ELEVATED TEMPERATURE CURING POLYMER COMPOSITIONS
USEFUL FOR AQUEOUS BASED PAINTS AND WOOD COATINGS

Background of Invention

5 The field of art to which this invention pertains is coating compositions useful as aqueous based paints or wood coatings which cure at ambient and elevated temperatures.

10 Coating compositions which cure under ambient conditions have been known for a long time. The earliest of such coating compositions are coatings based on drying oils which cure by air oxidation. Other coating compositions which have been developed more recently are those based on the epoxide-carboxylic acid reaction, isocyanate-moisture reaction, polyaziridine-carboxylic acid
15 reaction, and activated methylene-unsaturated acrylic reaction.

In U.S Patent No. 3,554,987, film forming interpolymers of acrylic acid, acetoacetoxyethyl methacrylate and monomers copolymerized therewith are described.

20 In U.S. Patent No. 4,408,018, polymers containing pendant acetoacetate moieties are mixed with polyacrylates which contain more than one unsaturated acrylic group and are cured through Michael addition using a strong base as catalyst.

25 Crosslinking through Michael addition is also shown in European Patent Application No. 227,454. In this patent application, compounds containing a plurality of pendant acetoacetate groups are blended with compounds containing a plurality of ethylenically
30 unsaturated acrylic groups and are cured with the addition of a strong base or an organometallic compound.

South African Patent No. 85-2044 describes coating compositions

curable at ambient temperatures made from a composition containing a plurality of activated methylene groups and ethylenically unsaturated carbonyl groups.

- 5 In an article by A. Noomen, entitled "Ambient Temperature Curable Coatings Based on Two-Pack Binders", Organic Coatings Conference, Athens, Greece-June, 1987, coating compositions which cure through the Michael addition reaction of acetoacetate- ketimine groups and acrylic-malonate groups are discussed.

10

Thermosetting coating compositions based on the epoxide- carboxylic acid reaction are disclosed in U.S. Patent Nos. 3,305,601, and 4,028,294 and European Patent Application No. 226,171.

- 15 Commonly owned U.S. Patent No. 4,906,684 is directed to ambient temperature curing polymer compositions containing acetoacetoxyethyl (meth)acrylate, glycidyl (meth)acrylate, a polymerizable acid and a copolymerizable monomer. When applied as a coating to a substrate, the coating self cross-links and cures at
20 ambient temperatures. These compositions are sold under the AMBICURE® resin trademark by Rhône-Poulenc Inc.

- Due to the ever increasing demand for decorative and protective coatings which will withstand a wide variety of uses and will hold
25 up under all kinds of environmental conditions, there is continuing need for new coating compositions.

Summary of the Invention

- 30 This invention is directed to ambient and elevated temperature curing coating latex (i.e., polymer dispersed in water) compositions. In one aspect, this invention pertains to coating compositions which contain an acetoacetoxy group, a glycidyl group and a carboxylic acid group. In another aspect, this invention
35 relates to film forming acrylic polymers which contain pendant

acetoacetoxy groups, glycidyl groups, and carboxylic acid groups.

The coating compositions of this invention are comprised of a polymer latex of (a) acetoacetoxyethyl acrylate or methacrylate; (b) glycidyl acrylate or methacrylate; (c) an ethylenically unsaturated polymerizable acid and (d) a monomer copolymerizable therewith, wherein the total weight percent of (a), (b) and (c) in the polymer is at least about 3 percent and not more than about 60 weight percent of the total amount of polymer solids in the latex, wherein (d) is present in the amount of about 40 to about 97 weight percent of the total amount of polymer solids in the latex and wherein the pH of the dispersion is about 7.5 to about 10.

When applied as a coating to a substrate, the coating cures at room temperature to a thermoset state. The coating is particularly preferred for use in aqueous based paints and in wood coatings.

Description of the Invention

Component (a), the acetoacetoxyethyl acrylate or methacrylate monomer used in this invention can be made by the reaction of diketene with hydroxyethyl acrylate or methacrylate. The acetoacetoxyethyl group contains a methylene group between the two carbonyls and due to this position is said to be an "active" methylene group. Such groups are capable of Michael addition across double bonds and can react with epoxide groups. In the preferred embodiment, the amount of this component in the aqueous dispersion ranges from about 0.5 to about 20 weight percent.

Component (b), the glycidyl acrylate or methacrylate monomers used in this invention are well known commercially available monomers. Such monomers can be made by the esterification of acrylic or methacrylic acid with glycidol or with epichlorohydrin followed by dehydrohalogenation. The glycidyl group is capable of reacting with active methylene groups, with carboxylic acid groups and with

other epoxide groups. In the preferred embodiment, the amount of this component in the aqueous dispersion ranges from about 1.0 to about 15.0 weight percent.

5 Component (c) comprises polymerizable acid monomers which are well known mono or polycarboxylic acids which contain one polymerizable bond per molecule. Generally such acids will contain from 3 to about 24 carbon atoms and one or two carboxylic acid groups per molecule. Examples of such acids are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, ethacrylic acid, 10 crotonic acid, citraconic acid and half esters of the dicarboxylic acids wherein the esterified alcohol group contains from 1 to about 20 carbon atoms. Examples of suitable half esters are methyl hydrogen fumarate, benzyl hydrogen maleate, butyl hydrogen maleate, 15 octyl hydrogen itaconate, dodecyl-hydrogen citraconate, and the like. The preferred acids for use in this invention are acrylic and methacrylic acid. In the preferred embodiment, the amount of this component in the aqueous dispersion ranges from about 0.5 to about 3.0 weight percent.

20 Component (d) comprises copolymerizable monomers which can be used in this invention together with the three classes of monomers referred to hereinabove and are any of the well known monomers which contain one ethylenically unsaturated polymerizable group per molecule and are copolymerizable with the other monomers. The 25 amount of this component in the dispersion ranges from about 40 to about 97 weight percent of the polymer solids, with a range of between about 60 and about 90 weight percent being most preferred. Any monomers which are copolymerizable with components (a), (b) and 30 (c) can be used in this invention. Such monomers are those which contain no groups which are reactive under polymerization conditions with acetoacetoxy groups, glycidyl groups, or carboxylic acid groups.

35 The types and amounts of copolymerizable monomers used in this

invention will vary depending on the particular end use for which the product of this invention is intended. Such variations are well known and can be readily determined by those skilled in the art. Preferred comonomers for use in this invention are the acrylate and methacrylate esters wherein the ester group is an alkyl group containing 1 to 8 carbon atoms.

Examples of such monomers are acrylic and methacrylic esters wherein the ester group contains 1 to about 20 carbon atoms, e.g., methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl methacrylate, decyl acrylate, lauryl methacrylate, benzyl acrylate, and the like.

Other acrylic or methacrylic esters which can be used in this invention are multifunctional acrylates or methacrylates, e.g., ethyleneglycol dimethacrylate, hexanediol diacrylate, etc. Such esters can be used in amounts up to about 5 weight percent based on the total weight of the monomers.

Other copolymerizable monomers are vinyl aromatic monomers, such as styrene, vinyl toluene, alpha methyl styrene and the like as well as nitriles and amides, e.g., acrylonitrile and acrylamide.

Additional copolymerizable monomers that can be used in this invention are the derivatives of the hypothetical vinyl alcohol, i.e., aliphatic vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, the vinyl ester of versatic acid and the like.

The compositions of this invention are prepared by polymerization of monomers emulsified in water using conventional emulsion polymerization procedures. These procedures can either take place in a continuous, batchwise, stepwise or semicontinuous mode.

Surfactants which are used for emulsification of the monomers are

anionic and nonionic surfactants and mixtures thereof.

5 Examples of useful anionic surfactants are organosulfates and
sulfonates, e.g., sodium and potassium alkyl, aryl and alkaryl
sulfates and sulfonates, such as sodium 2-ethylhexyl sulfate,
10 potassium 2-ethylhexyl sulfate, sodium nonyl sulfate, sodium
lauryl sulfate, potassium methylbenzene sulfonate, potassium
toluene sulfonate and sodium xylene sulfonate; higher fatty
alcohols, e.g., stearyl, lauryl, etc., which have been ethoxylated
and sulfonated; dialkyl esters of alkali metal sulfosuccinic acid
15 salts, such as sodium diamyl sulfosuccinate, and sodium dioctyl
sulfosuccinate; formaldehyde-naphthalene sulfonic acid condensation
products; and alkali metal salts, partial alkali metal salts and
free acids of complex organic phosphate esters.

15 Examples of nonionic surfactants which can be used in this
invention are polyethers, e.g., ethylene oxide and propylene oxide
condensates which include straight and branched chain alkyl and
alkaryl polyethylene glycol and polypropylene glycol ethers and
20 thioethers; alkylphenoxypoly(ethyleneoxy) ethanols having alkyl
groups containing from about 7 to about 18 carbon atoms and having
from about 4 to about 240 ethyleneoxy units, such as
heptylphenoxy-poly(ethyleneoxy)ethanols, nonylphenoxy-
poly(ethyleneoxy)ethanols; the polyoxy-alkylene derivatives of
25 hexitol (including sorbitans, sorbides, mannitans and mannides);
partial long chain fatty acid esters, such as the polyoxyalkylene
derivatives of sorbitan monolaurate, sorbitan monopalmitate,
sorbitan monostearate, sorbitan tristearate, sorbitan monooleate
and sorbitan trioleate; the condensates of ethylene oxide with a
30 hydrophobic base, said base being formed by condensing propylene
oxide with propylene glycol; sulfur containing condensates, e.g.,
those prepared by condensing ethylene oxide with higher alkyl
mercaptans, such as nonyl, dodecyl, or tetradecyl mercaptan, or
with alkylthiophenols wherein the alkyl group contains from about
35 6 to about 15 carbon atoms; ethylene oxide derivatives of long

chain carboxylic acids, such as lauric, myristic, palmitic, or oleic acids or mixtures of acids, such as tall oil fatty acids; and ethylene oxide derivatives of long chain alcohols such as octyl, decyl, lauryl, or cetyl alcohols.

5

The amounts of surfactants employed in the emulsion polymerization process will range from about 0.01 to about 10 weight percent, preferably between about 0.2 and about 5 weight percent based on the total weight of monomers and water.

10

In addition to the surfactants, the emulsion polymerization system can also contain protective colloids. Examples of protective colloids are ether linkage-containing protective colloids, such as hydroxymethyl cellulose, hydroxyethyl cellulose, ethylhydroxyethyl cellulose, carboxymethyl cellulose, ethoxylated starch derivatives and the like. Other protective colloid substances can also be used either alone or together with the ether linkage containing materials. Other such protective colloids include partially and fully hydrolyzed polyvinyl alcohols, polyacrylic acid, sodium and other alkali metal polyacrylates, polyacrylamide, poly(methyl vinyl ether/maleic anhydride), polyvinylpyrrolidone, water soluble starches, glue, gelatin, water soluble alginates, such as sodium or potassium alginate, casein, agar and natural and synthetic gums, such as guar, xanthan, gum arabic and gum tragacanth. The protective colloids can be used in amounts ranging from about 0.1 weight percent to about 2 weight percent based on the total weight of a polymer dispersion. Other surface active agents are clearly contemplated within the scope of the present invention.

30

The monomers used in this invention are preferably polymerized by means of a conventional free radical polymerization initiator or initiator system (which can also be referred to as an addition polymerization catalyst, a vinyl polymerization catalyst, or a polymerization initiator), preferably, although not necessarily, one which is substantially water soluble. Among such initiators

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are peroxides, such as hydrogen peroxide, tertiary butyl hydroperoxide, cumene hydroperoxide, alkali metal, (e.g., sodium, potassium or lithium) and ammonia persulfates, perphosphates, and perborates; azo nitriles, such as alpha, 5 alpha-azobisisobutyronitrile, and redox systems including such combinations as mixtures of hydrogen peroxide, t-butyl hydroperoxide or the like and any of the iron salts, titanous salts, zinc formaldehyde sulfoxylate, or sodium formaldehyde sulfoxylate; alkali metal or ammonium persulfate, perborate or 10 perchlorate together with an alkali metal bisulfite, such as sodium metabisulfite; and alkali metal persulfate together with an aryl phosphinic acid such as benzene phosphinic acid and the like. The amount of polymerization initiator employed will be no more than that required to obtain substantially complete monomer conversion at lower initiator cost. The amount of initiator will generally 15 vary from about 0.1 to about 1 percent by weight based on the weight of the monomers added.

The emulsification and polymerization reaction can be conducted by 20 any of the well known procedures which are used to prepare emulsion polymers. For instance, the monomers, catalysts, surfactants, protective colloids, if used, and chain transfer agents, e.g., alkyl mercaptans, if used, can all be added to the reactor, with suitable agitation to obtain emulsification at a temperature of 25 about 30°C to about 95°C until the polymerization is complete.

Alternatively, the reaction can be conducted by adding water, surfactants, and protective colloids, if used, into the reactor, raising the temperature to the reaction temperature and then adding 30 the monomers and a solution of the initiator to the reactor under agitation. Still another method is to pre-emulsify the monomers in a portion of the water and a portion of the surfactant along with initiator, and to add the pre-emulsion to the reactor which contains the remaining water and surfactant.

In order to obtain compositions which form coatings having superior coating properties when cured under ambient or elevated temperature conditions, in preferred embodiments the acetoacetoxy moiety, the glycidyl moiety and the acid moiety should be present in certain preferred ratios. It has been found that acetoacetoxy group and the glycidyl group should be present in a weight ratio of less than or equal to 0.5, wherein the weight ratios are calculated based on the weight of acetoacetoxyethyl (meth)acrylate and glycidyl (meth)acrylate. The glycidyl group and the carboxylic acid group should be present in a weight ratio greater than 1.0 wherein the weight ratios are based on the weight of glycidyl (meth)acrylate and the ethylenically unsaturated polymerizable acid(s). Furthermore, the total weight percent of the three monomers (components (a), (b) and (c)) used to form the polymer should be at least about 3 percent and not more than about 60 percent, said weight percents being based on the total weight of all monomers used to form the polymer.

The amount of water used to prepare the compositions of this invention will depend upon the solids content desired in the finished polymer latex. Generally the solids content will be between about 20 percent and about 70 percent by weight. Preferably the solids content will be between about 40 percent and about 60 percent by weight.

After the emulsion polymerization is complete, the pH of the latex is adjusted to about 7.5 to about 10 using a water soluble base. Suitable bases are alkali metal, ammonia and quaternary ammonium bases. Examples of suitable bases are ammonia, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, benzyltrimethylammonium hydroxide and the like. A particularly preferred base is tetramethylammonium hydroxide.

For use as paints or wood coatings, the polymer latex compositions

of this invention can be applied to a variety of substrates to form films and coatings which cure to thermoset compositions at ambient or elevated temperatures. Preferred curing temperatures range from about -10°C to about 100°C.

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A particularly suitable use for the inventive materials is in aqueous based paints. Such paints could be applied to many surfaces such as dry wall, wood, siding, metal, concrete, polymer surfaces, glass, and the like. When used in paints, final formulations may also include additives to provide enhanced performance. Examples of such additives include thickeners, defoamers, wet edge modifiers and glycols to prevent premature curing, coalescing agents, anti-blocking agents, pigments, base activator materials other specialty additives and the like. These additives typically comprise less than 5 percent by weight of the solids present in the final aqueous dispersion. In addition, by manipulating the amount of pigment volume concentration and total solids and additives in the coatings formula, different finishes of the paint ranging from matte to high gloss may be produced. Such finishes will be directly dependent on the final desired use for the paint.

When used, the inventive dispersions of the present invention, including the optional additives, are simply applied to a surface at a coating thickness ranging from about 1 mil to about 4 mils by using a brush, roller, or other means well known in the art. The dispersion is then allowed to cure at temperatures ranging from about 5°C to about 40°C, more preferably between about 5°C and about 25°C, and most preferably between about 5°C to about 15°C. Within about 12 hours after application, the dispersion begins to cross-link and form a cured film. The curing operation tends to be at least 85% complete after about 48 hours. The application procedure may be repeated to apply multiple coats of paint.

35 Another suitable use for the inventive materials is in wood

coatings. To the extent the term wood coatings is used, it is intended to encompass all types of wood and all forms of wood coatings such as furniture, commercial grade flooring, residential flooring, patio decks, contractor finished flooring, paneling, frames, molding, cabinets and the like. When used as a wood coating, the inventive aqueous dispersions may include additional additives to provide enhanced performance. Examples of such additives include thickeners, defoamers, wet edge modifiers and glycols to prevent premature curing, coalescing agents, pigments, base activator materials and the like. These additives typically comprise less than 5 percent by weight of the solids present in the final aqueous dispersion.

For use as a wood coating, the inventive dispersions of the present invention, including the optional additives are simply applied to a wood surface at a coating thickness ranging from about 1 mil to about 3 mils by using a brush, roller, or other means well known in the art. The dispersion is then allowed to cure at temperatures ranging from about 5°C to about 40°C, more preferably between about 5°C to about 15°C. Within about 12 hours after application, the dispersion begins to cross-link and form a cured film. The curing operation tends to be at least 85% complete after about 48 hours and results in a clear, colorless, glossy film.

In addition to providing desirable aesthetic and physical properties, the inventive coating materials possess far less volatile organic contents (VOC) than most, if not all, commercially available paints and wood coatings. As such, they are ideal commercial candidates.

The following examples describe the invention in more detail. Parts and percentages are by weight unless otherwise indicated.

The extent of cure of the films in the Examples is determined by testing for Gel Content and by calculating Swelling Index. These

determinations are made on films which had been left under ambient conditions for at least 48 hours. The films are removed from the substrate and tested as follows:

- 5 (1) duplicate samples of the films, approximately 2 gram samples, are weighed into glass bottles;
- (2) toluene, 75 ml, is added to each bottle, and the bottles are sealed and shaken vigorously;
- 10 (3) after 3 days, the bottle contents are decanted onto a weighed fine nylon mesh screen, and were thoroughly washed with toluene;
- (4) the mesh screen is weighed, then dried in a vacuum oven and
- 15 weighed; and
- (5) after determining the weight of wet gel and dry gel, the Gel Content and Swelling Index is determined as follows:

$$20 \quad \% \text{ Gel Content} = \frac{\text{wt. of dry gel} \times 100}{\text{wt of film}}$$

$$\text{Swelling Index} = \frac{\text{wt wet gel} - \text{wt dry gel}}{\text{wt dry gel}}$$

- 25 Gel Contents of at least about 95 percent and Swelling Indexes of less than 5 indicate satisfactorily cured films.

Example 1

- 30 To a suitable reactor fitted with two dropping funnels, condenser, agitator and thermometer were added 355 parts of water, 1.95 parts sodium bicarbonate and 9.83 parts of phosphated nonyl phenyl polyethylene glycol ether surfactant. To one dropping funnel were added 111.45 parts of methylmethacrylate, 128.57 parts of butyl

acrylate, 10 parts of acetoacetoxyethyl methacrylate, 7.5 parts of acrylic acid and 22.5 parts of glycidyl methacrylate. To the other dropping funnel were added 40.43 parts of water and 1.13 parts of ammonium peroxydisulfate. Agitation was begun and heat was applied raising the temperature in the reactor to 85°C. An initial charge of 0.06 part of ammonium peroxydisulfate in 19.5 parts of water was made to the reactor and the slow addition of monomers and catalyst was begun. While keeping the temperature at 85°C, the monomers were added over 2 hours and the catalyst over 2 hours and 5 minutes. The temperature was lowered to 70°C and 0.3 part of t-butylhydroperoxide was added. The temperature was then lowered to 35°C and a solution of 0.3 part of sodium formaldehyde sulfoxylate in 9.89 parts of water was added. When the temperature reached 25°C, 4.89 parts of 28 percent ammonium hydroxide and 1.18 parts of a microbiostat were added. The resulting stable latex had a viscosity of 25 cps, a solids content of 40.45 percent and a pH of 5.2.

The pH of a portion of the latex was adjusted with ammonia to 7.5 and then with sodium hydroxide to 9.0. (Ex 1A). Another portion had the pH adjusted to 9.0 with tetramethyl ammonium hydroxide (Ex 1B). Films were drawn down on glass panels and were left under ambient conditions for 48 hours. The films were removed from the substrate and tested with the results shown in Table 2.

Example 2

Using the same procedure described in Example 1, 143.76 parts of methyl methacrylate, 165.79 parts of butyl acrylate, 9.03 parts of methacrylic acid, 14.45 parts of acetoacetoxyethyl methacrylate and 28.9 parts of glycidyl methacrylate were polymerized. The resulting latex had a viscosity of 1100 cps and a solids content of 47.32 percent. The pH of the latex was adjusted to 9.0 with tetramethyl ammonium hydroxide. Films were drawn down on glass panels and were left at ambient conditions for 48 hours. The film withstood 108 methyl ethyl ketone double rubs. The results of other film tests are shown in Table 2.

Example 3

Using the same procedure described in Example 1, 111.49 parts of methylmethacrylate, 128.57 parts butyl acrylate, 5.01 parts of acrylic acid, 7.42 parts of acetoacetoxyethyl methacrylate, and 10.2 parts of glycidyl methacrylate were polymerized. The resulting latex had a viscosity of 27.5 cps, a solids content of 40.74 percent and a pH of 7.45. The pH of the latex was adjusted to 7.5 with ammonia and to 9.0 with sodium hydroxide. Films made from the latex were tested after 48 hours under ambient conditions. The test results are shown in Table 2.

Example 4

Using the same procedure described in Example 1, a latex was made by polymerizing 111.49 parts of methyl methacrylate, 128.57 parts of butyl acrylate, 5.02 parts of acrylic acid and 22.06 parts of acetoacetoxyethyl methacrylate. The latex had a viscosity of 22.5 cps, a solids content of 39.88 % and a pH of 7.38. The pH of the latex was adjusted to 7.5 with ammonia and to 9.0 with sodium hydroxide. Films made from the latex were tested after 48 hours under ambient conditions. The test results are shown in Table 2.

Example 5

Using the same procedure described in Example 1, a latex was made by polymerizing 142.13 parts of methyl methacrylate, 163.87 parts of butyl acrylate, 6.4 parts of acrylic acid and 19 parts of glycidyl methacrylate. The latex had a viscosity of 147.5 cps, a solids content of 45.74 percent and a pH of 7.4. The pH was adjusted to 9.0 with ammonia and sodium hydroxide. Films made from the latex and were tested after 48 hours under ambient conditions. The test results are shown in Table 2.

Example 6

Using the same procedure described in Example 1, a latex was made using 145.8 parts of methyl methacrylate, 168.1 parts of butyl acrylate, and 9.83 parts of acrylic acid. The latex had a viscosity of 1650 cps and a solids content of 45.34 percent and a pH of 7.3. The pH of a portion of the latex was adjusted to 7.3 with ammonia. Another portion had the pH adjusted to 9.0 with tetramethylammonium hydroxide (TMAH). Films made from the latex were tested after 48 hours at ambient conditions. The film made from the portion containing TMAH withstood 38 methyl ethyl ketone double rubs. The test results are shown in Table 2.

Example 7

Using the same procedure described in Example 1, a latex was made by polymerizing 153.11 parts of methyl methacrylate, 176.47 parts of acetoacetoxyethyl methacrylate and 21.73 parts of glycidyl methacrylate. The latex had a viscosity of 75 cps and a solids content of 39.88 percent. The pH of the latex was adjusted to 9.0 with tetramethylammonium hydroxide. Films made from the latex were tested after drying for 48 hours under ambient conditions. The test results are shown in Table 2.

Example 8

Using the same procedure described in Example 1, a latex was made by polymerizing 120 parts of methyl methacrylate, 138.74 parts of butyl acrylate, and 8 parts of acrylic acid. The latex had a viscosity of 20 cps and a solids content of 40.38 percent. The pH was adjusted to 8.5 with tetramethylammonium hydroxide. Films made from the latex were tested after drying for 48 hours under ambient conditions. The test results are shown in Table 2.

Example 9

Using the same procedure described in Example 1, a latex was made by polymerizing 39.04 parts of methyl methacrylate, 110.84 parts of methyl methacrylate, 18.35 parts of methacrylic acid, 45.85 parts of acetoacetoxyethyl methacrylate and 91.76 parts of glycidyl methacrylate. The resulting latex had a viscosity of 15 cps at 40.96 percent solids. The pH was adjusted to 8.5 with tetramethylammonium hydroxide. Films made from the latex were tested after drying for 48 hours under ambient conditions. Test results are shown in Table 2.

Table 1

Monomer Content

	Ex	AAEM %	GMA %	MAA/ AA %	Other Monomer %
5					
	1	3.5	8	2.5	86
	2	4	8	2.5	85.5
10	3	3	4	2	91
	4	8	-	2	90
	5	-	6	2	92
	6	-	-	3	97
	7	3	6	-	91
15	8	-	-	3	97
	9	15	30	6	49

AAEM - acetoacetoxyethyl methacrylate

GMA - glycidyl methacrylate

20 MAA - methacrylic acid

AA - acrylic acid

Table 2

Ex.	Gel Content %	Swelling Index	Tensile psi	Elong %
1A	96.13	4.02	1149	182
1B	96.34	2.98	1019	173
2	97.5	2.58	1581	123
3	95.09	6.61	814	277
4	91.2	8.39	940	265
5	92.31	8.2	1118	239
6*	83.82	28.66	871	376
6**	79.75	30.56	384	475
6***	97.08	3.03	1333	143
7	88.28	8.47	783	317
8	79.75	30.56	384	475
9	97.2	1.04	2200	5

- 5 * Example 6 neutralized with ammonia - pH 7.3
 ** Example 6 neutralized with TMAH - pH 9.0
 *** Example 6 blended with polyaziridine - (2%W/W) - Xama 7 from Sannacor Industries.

- 10 Coatings made from the compositions of this invention are Examples 1, 2, 3 and 9.

Example 10

15

To a suitable reactor fitted with condenser, agitator, thermometer,

and two metering pumps, is added 431 parts water, 10.28 parts of phosphated nonylphenyl polyethylene glycol surfactant, and 1.98 parts sodium bicarbonate. Agitation is begun, and heat is applied, raising the temperature to 75°C. An initial charge of 0.07 parts ammonium persulfate is added. While maintaining the temperature at 75°C, a mixture of monomers comprising 1.97 parts ethylene glycol dimethacrylate, 24.99 parts acetoacetoxyethyl methacrylate, 49.57 parts glycidyl methacrylate, 50.92 parts styrene, and 66.99 parts butyl acrylate is pumped into the reactor over a period of 2 hours and 30 minutes. Simultaneously, an initiator solution comprising 0.59 parts ammonium persulfate and 21.12 parts water is pumped into the reactor over 2 hours and 45 minutes. 45 minutes after the completion of this initiator addition, addition of a second portion of initiator solution, comprising 0.59 parts ammonium persulfate and 21.15 parts water is begun, also lasting 2 hours and 45 minutes. Along with this second initiator addition, a second monomer mixture is pumped into the reactor comprising 4.13 parts acrylic acid, 1.88 parts methacrylic acid, 59.44 parts methyl methacrylate, and 129.74 parts ethyl acrylate over 2 hours and 20 minutes. After all initiator and monomer mixtures are added, the temperature is maintained at 75°C with agitation for a further 45 minutes. The temperature is lowered to 70°C, and 0.5 parts of t-butyl hydroperoxide solution (70% active) is added. After further cooling to 35°C, a solution of 0.5 parts sodium metabisulfite and 10 parts water is added. The pH of the latex is adjusted to 8.5 with 10% tetramethyl ammonium hydroxide. The Gel Content of the latex is 96.0, the Swelling Index is 3.3, the Tensile Strength is 2000 psi, the percent Elongation is 180 percent, the viscosity is 100 cps, the percent solids level is 43% and the minimum film forming temperature is 10°C.

TEST DATA-PAINTS

A white high gloss paint formulation is produced by dispersing 580.0 parts of the composition of Example 10, 2.0 parts of dioctyl

sodium sulfosuccinate (Pentax 99, sold by Rhône-Poulenc Inc.), 14.0 parts of Rheolate 300, a thickener sold by Rheox, Inc., 4.0 parts of ammonium hydroxide, 12.0 parts of a tri-propylene glycol methyl ether coalescent (Dowanol TPM, sold by Dow Chemical Company) and 4.0 parts of Foamex 1488 (a defoamer sold by Tego Chemie Service USA) into a medium comprising 170.0 parts water, 9.0 parts of Colloid 111, an anionic dispersant sold by Rhône-Poulenc Inc., 2.0 parts of a modified alkylphenoxy-poly (ethyleneoxy) ethanol nonionic surfactant sold by Rhône-Poulenc Inc., 1.0 parts of 2-amino-2-methyl-1-propanol containing 5% water (AMP-95 sold by Angus Chemicals, Northbrook, IL), 25.9 parts propylene glycol, 2.0 parts of Foamex 1488 and 180.0 parts of Ti-Pure R700, a rutile pigment sold by E.I. Dupont. This paint formulation has a density of 9.93 lbs/gal and a VOC (volatile organic content) level of less than 50.0 g/L. The percentage solids of the formulation is 45.4 percent by weight or 34.6 percent by volume, the percent PVC is 15.2, the pH is 8.9, the Stormer Viscosity is 100 KU \pm 2, and the ICI Cone & Plate Viscosity is 0.70 P \pm 0.05.

The following properties of this inventive formulation are measured:

1) Gloss at 60° and 20° is measured by using ASTM Test D-523. The values for gloss at the respective angles of measurement are 86/61.

2) Sag Resistance is measured using ASTM Test D-4400. The measured value is 10 mils.

3) Levelling is measured using ASTM Test D-4062, with a score of 9 being best. The value for the inventive formulation measured is 9.

4) Wet adhesion to gloss alkyd paint is measured using ASTM Test D-3359. The adhesion is excellent. Its value is

measured at 10.

5 The above data demonstrates that the inventive paint formulation
which incorporates the latex of Example 10 exhibits excellent
gloss, block resistance, wet adhesion and other film properties.
In comparison to other commercially-available products for similar
market applications, the inventive formulations equal or exceed the
10 performance of such commercial products. More over, the VOC of the
inventive formulation is less than 50 g/L, which is far superior to
commercial formulations, which typically have a VOC of between
about 350 and about 380 g/L.

TEST DATA-WOOD COATINGS

15 A clear gloss wood coating formulation is produced by dispersing
667 parts of the composition of Example 10 along with one part of
a dioctyl sodium sulfosuccinate into a medium comprising 169.6
parts water, 4 parts of Rheolate 300, a thickener sold by Rheox
20 Inc., 2.2 parts of Colloid 652, a defoamer sold by Rhône-Poulenc
Inc., 25.9 parts of propylene glycol which functions as a wet edge
modifier, and 5.7 parts ammonium hydroxide. This formulation has
a VOC (volatile organic content) level of 34.0 g/L. The percentage
solids of the formulation is 35.2 percent by weight or 32.5 percent
25 by volume. The Stomper viscosity of the formulation is 61 ± 3KU.

This formulation is compared to two commercially available products
which are sold for use as wood coatings. The following properties
for both the inventive formulation as well as the commercial
30 products are measured:

- 1) VOC in grams per liter
- 2) Percentage by weight of nonvolatiles

35

3) Gloss at 60° and 20° is measured by forming a 3 mil film using a draw down applicator system on a Leneta Form 2C Card

4) Pencil hardness is measured using ASTM Test D-3363

5) Freeze/Thaw Stability is measured using ASTM Test 2243

6) Dry time is measured from the time of application until it is dry to the touch when drawing down the coating composition on a Leneta Form 2C Card at 72°F, 47% relative humidity

7) Gloss at 60° and 20° on poplar wood - the wood coating formulations are applied with a nylon brush onto poplar wood and are dried. This procedure is repeated at two hour intervals until three full coats have been applied. Thereafter, a gloss reading is measured twenty-four hours after the last coat has been applied.

8) Imprint resistance is determined by placing a porcelain coffee cup containing 175 grams of 175 °F water onto a coated surface for ten minutes. The cup is removed and the surface is qualitatively evaluated to see if there is any imprint resistance. A score of ten defines excellent imprint resistance.

9) Chemical/solvent resistance: the resistance of the coating composition to several solvents and household chemicals is measured by applying three (3) drops of each solvent onto the coating, covering the solvent with a watch glass for four (4) hours, removing both the watch glass and the test media, and qualitatively analyzing the sample on a scale from 0 to 10 with 10 being best. The following solvents and household chemicals are utilized and the scores for each are added together to obtain the value shown in Table 3: water, vodka, Fantastik® cleaner, nail polish remover,

acetone-free nail polish remover, coffee, tea, lemon juice, catsup, mustard, 10% sodium hydroxide and red wine.

Results of the above tests are shown in Table 3.

5	<u>Table 3</u>			
		<u>Inventive Formulation</u>	<u>Commercial Product A</u>	<u>Commercial Product B</u>
10	VOC (g/L)	34.0	< 350	< 300
	Nonvolatiles (% wt.)	35.4	34.0	32.0
15	Gloss, 60°/20° 3 mil	86/62	89/54	94/66
20	Pencil Hardness	6B	2B	4B
25	Freeze/Thaw Stability (cycles passed)	5	5	5
	Dry Time (Through, min.)	3.5	> 10	5.0
30	Gloss, 60°/20°, Poplar, with grain 3 coats	66/15	58/10	66/14
35	Imprint Resistance (10=best, 0=worst)	10	9	10
40	Chemical/Solvent Resistance Maximum = 120	92	82	92

- 5 The above data demonstrates that the inventive formulation which incorporates the latex of Example 10 performs comparably, if not better, than the two commercial products. Moreover, the inventive formulation has a very low VOC, and as such is more environmentally desirable than either of the commercial products.
- 10 The principles, preferred embodiment and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as
- 15 illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

ABSTRACT

The invention relates to two-component polyurethane systems, consisting of one polyol component and one isocyanate component. Said polyol component contains at least two amines A1 and A2, the reactivity R1 of amine A1 with isocyanate being considerably greater than the reactivity R2 of amine A2 with isocyanate. As a result, two time-delayed reactions take place. This gives the inventive systems the desired low level of viscosity, and the thixotropic properties that prevent even thick layers from sloughing off of vertical surfaces. The inventive two-component polyurethane systems can be used for producing cubing models, master models and the like in the automobile industry and for producing structured bodies and thick coatings and sealing beads.

PATENT CLAIMS

1. Two-component polyurethane system comprised of a polyol component and an isocyanate component, which react exothermically, thereby characterized, that the polyol component comprises at least two amines A1 and A2, wherein the reactivity R1 of amine A1 to the isocyanate component is greater than the reactivity R2 of amine A2, wherein amine A1 is so selected, that it reacts with the isocyanate component within a few seconds for transformation to such a structural viscosity, that the system is not fully cured but is non-flowing and wherein amine A2 is so selected, that its reaction with the isocyanate component is delayed with respect to that of amine A1, so that an increased thermally stable structural viscosity is produced.
2. Two-component polyurethane system according to Claim 1, thereby characterized, that the relationship of the reactivity R1 of amine A1 to reactivity R2 of amine A2 with respect to the isocyanate component is from 1000 to 5.
3. Two-component polyurethane system according to Claim 2, thereby characterized, that the relationship of the reactivity R1 of amine A1 to the reactivity R2 of amine A2 with respect to the isocyanate component is from 100 to 5.
4. Two-component polyurethane system according to Claims 1-3, thereby characterized, that amine A1 is selected from aromatic amines (Group 1 a), cycloaliphatic amines (Group 1 b), araliphatic amines (Group 1 c), and aliphatic amines and polyamines (Group 1 d).
5. Two-component polyurethane system according to Claims 1-3, thereby characterized, that amine A2 is selected from Group 2 which includes:
methylene-bis-(3-chlor-2,6-diethylanilin) (M-CDEA),

3,5-dimethylthio-(2,4 or 2,6)-toluylenediamine,
3,5-diamino-4-chlor-benzoesaure-isobutylester (DACB),
methylene-to-anthranilate methylester (MBMA),
4,4'-diamino-3,3'-dichlordiphenylmethane (MOCA)
and similar compounds.

6. Two-component polyurethane system according to one of Claims 1-5, thereby characterized, that amine A1 is selected from Group 1 a) through 1 d) and amine A2 is selected from Group 2.
7. Two-component polyurethane system according to one of Claims 1-5, thereby characterized, that amine A1 is selected from Groups 1 b) through 1 d) and amine A2 is selected from Group 1 a), wherein the reactivity R1 of amine A1 from Groups 1 b) through 1 d) is greater than the reactivity R2 of amine A2 from Group 1 a).
8. Two-component polyurethane system according to one of Claims 1-7, thereby characterized, that amine A1 is 4,4'-diamino-3,3'-dimethyl-cyclohexylmethane and amine A2 is 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline).
9. Two-component polyurethane system according to one of Claims 1-8, thereby characterized, that the weight relationship of amine A1 to amine A2 is 0.5:1 to 2:1 in wt.%.
10. Two-component polyurethane system according to one of Claims 1-8, thereby characterized, that amine A1 comprises

0.25 to 5 wt.% of the total polyol component and amine A2 comprises 0.3 to 5 wt.% of the total polyol component.

11. Two-component polyurethane system according to one of Claims 1-10, thereby characterized, that the polyol is at least one of a polyether polyol and a polyester polyol with a molecular weight in the range of 75 to 6000, and the diisocyanate is a 4,4'-diphenylmethane-diisocyanate-derivative.
12. Process for production of the two-component polyurethane system according to the preceding claims, thereby characterized, that the amine component is dissolved in the polyol component, the two amine components and the desired additives are added using a stirring device and the resulting mixture is mixed with the diisocyanate in a mixing-and-dosing device.
13. Use of the two-component polyurethane system according to the preceding claims for production of shaped bodies for cubing-models, prototypes and the like in the automobile industry, as well as for production of structured bodies and thick coatings and sealing beads.